INVESTIGATION OF SUPERCRITICAL CO$_2$ SORPTION BY POLYSTYRENE AND FORMATION OF POROUS STRUCTURES

Nikolaev A.[1], Nikitin L.[2]*, Gallyamov M.[1], Vinokur R.[2], Said-Galiyev E.[2], Khokhlov A.[1,2], Schaumburg K.[3],

[1]Physics Department of Lomonosov Moscow State University, Vorobievy gory, 119992 Moscow, Russia
[2]Nesmeyanov Institute of Organoelement Compounds, 119991 Vavilov Str., 28, Moscow, Russia, e-mail: lnik@ineos.ac.ru, Fax: 7(095)1355085
[3]Centre for Interdisciplinary Studies of Molecular Interactions, Department of Chemistry, Roskilde University, Universitetsvej 1, Roskilde DK-4000, Denmark

Sorption of supercritical (sc) CO$_2$ by polystyrene (PS) was studied in situ. Diffusion coefficients of CO$_2$ in PS were determined both analyzing the optical boundaries movement and gravimetric technique. Temperature and pressure dependencies of diffusion coefficients were obtained. The non-monotone pressure dependences of diffusion coefficients were discussed. Obtained results provided more information about concentration dependencies of CO$_2$ diffusion coefficients in PS.

These results were applied to investigation of processes of porous structure formation in PS during desorption. Different morphology of porous structures in polymer samples were produced in sc CO$_2$ desorption process after preliminary exposition under supercritical conditions. Morphology of obtained porous structures were examined by optical microscopy. The dependencies of pores sizes on exposition time, pressure, temperature and pressure release rate were obtained. Non-uniform pores size distributions were detected at various experimental conditions. Optimal conditions for the different porous structure formation were determined. It was shown that by modification of exposition conditions it is possible to obtain controlled porous structure with non-uniform porosity morphology.

INTRODUCTION

The behavior of various classes of polymers in supercritical fluids, especially in supercritical carbon dioxide, has become a subject of considerable interest in recent years [1]. This increased attention is due to the fact that supercritical CO$_2$ is a solvent or plasticizer for a variety of polymers, having such advantages over conventional solvents (plasticizers) as low cost, environmental friendliness, incombustibility, and ease of removal from a polymer after completion of a process.

On the other hand, the interest concerning this fluid is due to the possibility of altering the morphological and functional properties of polymers by holding them in supercritical CO$_2$ and the ability of the latter to extract low-molecular-mass compounds including water, residual solvents, and monomers from polymer. In addition, the possibility of forming a porous structure in polymers by varying the pressure and temperature of supercritical CO$_2$ upon exposure and decompression seems quite promising as it can be used to manufacture porous adsorbents, filters, membranes, etc. materials.

Prevailing method of producing porous materials is based on the solution temperature quench with following solution quality decrease and fase separation induction [2]. Alternative

is a method consisted of polymer exposition in sc CO_2 under constant pressure and temperature with subsequent decompression under constant temperature. This method is based on significant decrease of glass transition temperature T_g [3] for various polymers in the presence of CO_2 at elevated pressures. During decompression amount of CO_2 in polymer decreases and T_g rises. Polymer vitrificates and porous structures stop generated [4]. In this work we have investigated porous structures generated at different experiment conditions.

However, successful implementation of such technologies in practice requires detailed study both of swelling mechanisms and pore formation upon sorption and desorption of supercritical fluid CO_2.

The swelling of poly(dimethylsiloxane)s in the high elastic state in supercritical CO_2 was studied by Royer et al. [5]. The equilibrium swelling degrees and diffusion coefficients were determined by monitoring the dynamics of displacement of the physical boundary of a swelling polymer placed in a test tube. Von Schnitzler and Eggers [6] analyzed the mass and volume swelling kinetics in supercritical CO_2 for PET samples in the form of extended cylinders, determined the equilibrium diffusion coefficients, and measured sorption isotherms.

In this work, we studied swelling of parallelepiped-shaped polystyrene (PS) samples in supercritical CO_2 and analyzed the kinetics of movement of the optical boundaries formed in the samples during the sorption of CO_2.

MATERIALS AND EQUIPMENT

Swelling of polystyrene in supercritical carbon dioxide was studied *in situ*. Experiments were carried out in a high-pressure cell furnished with an optical channel. This allowed to measure the dynamics of diffusion front propagation in the polymer samples during the swelling process by the use of an optical m icroscope supplied with a digital video camera.

We deal with the samples of the PS (purchased from Aldrich Chemical Co., molecular mass M_n=140000, M_w=230000; density 1.04 g/cm^3), in a form of parallelepipeds (which were prepared by fashion from PS granules and additional polishing procedure). A high-purity CO_2 (> 99.997%, 0.0002% O_2, 0.001% H_2O) was used as received.

The experimental set-up was described in [7]. A syringe press with 150 ml volume was used to generate the pressure up to 25 MPa. A system of valves allowed CO_2 access to the reaction cell. The pressure generator and the reaction cell line were equipped with mechanical manometers for pressure control upon the inlet and outlet of CO_2. The reaction cell was also supplied with electronic sensors of pressure and temperature. The designed high-pressure cell has an inner volume of approximately 10 cm^3 and is made of stainless steel. The wall thickness is several times greater than the calculated limiting values for pressure range used (up to 25 MPa). This allowed the heaters, capillary inlets, and temperature sensor to be built in the cell bulk. The adaptive proportional-integral-differential temperature control allows to set a precision better than ±0.2 °C. Experiments were carried out in temperature range 38-65 °C. Indium sealed 10 mm thick quartz glass or sapphire optical windows were used to realize the optical channel in the high-pressure cell. *In situ* observations of the polymer samples sorption process were performed with an optical microscope equipped with a Logitech digital camera. The information was recorded as raster images (640×480 pixels) onto the computer hard drive at fixed time intervals. A super-bright light emitting diode was used for lighting. The set-up was controlled by a personal computer (Pentium III-750 MHz, RAM 128 MB), provided with the data acquisition board "DT-322" (Data Translation Inc., USA). Original software was developed to control the experiment in real-time regime.

For comprehensive investigation of morphology of obtained structures it was used microtome Leica RM2145. This device allowed to produce sample sections with thickness up to 0.25 mcm. To attach samples in microtome they were placed in to special forms and pour with mounting mixture. Cuts were carried out with spacing of 1.5 mcm parallel to one of the sample edge. In addition, images of the sample cuts were obtained using optical microscope "Zeiss" with magnification of 420. With the help of digital video camera LCL-902 HS "Watec America Corp., USA" images with the resolution of 480x360 points were recorded on to the computers hard drive.
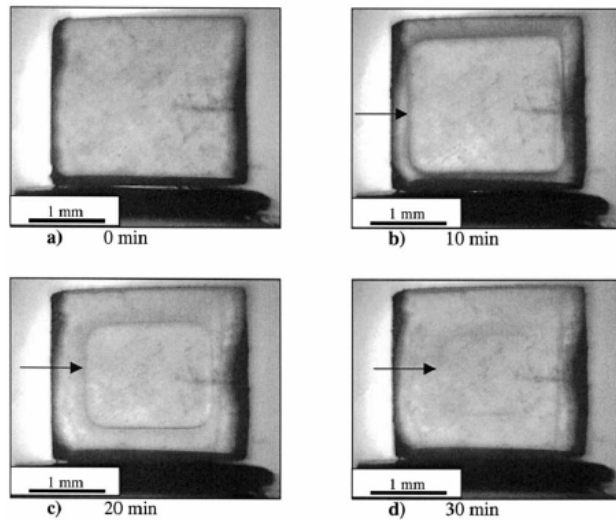
RESULTS AND DISCUSSION

Figure 1 a-d. In situ images of sc CO_2 sorption stages in PS in a high-pressure cell at t = 65°? , P = 25 MPa. Visible sample dimensions are 3.1×2.7 mm^2. The arrow depicts the position of the diffusion front

Fig. 1 shows the images of the PS sample inside the high-pressure cell. The propagation of the CO_2 diffusion fronts in polystyrene can be clearly seen.

In situ observation of the front propagation allows determination of the diffusion coefficient *D*. For sorption behavior of a polymer sample in the case of constant sorbate concentration the square of the diffusion front propagation distance, X^2, is directly proportional (at the initial stage of Fickian diffusion) to the time *t*, while the constant of proportionality is determined by the diffusion coefficient *D*:

$$X^2 = \alpha Dt, \qquad (1)$$

where $\alpha \tilde{} 3$, as it was estimated from the experimental data for swelling polymer sample [8]. Thus, the experimental data for the square of the optical boundary of the front propagation distance X^2 versus time *t* are expected to form a straight line with the slope ratio proportional to *D*.

The typical results of propagation kinetics of the optical boundaries of diffusion fronts in PS samples are plotted in Fig. 2. It is clear that the distance of the optical boundaries propagation squared versus time can be well fitted with a linear function. The Eq. (1) allows to determine the diffusion coefficient *D*.

The typical results of propagation kinetics of the optical boundaries of diffusion fronts in PS samples are plotted in Fig. 2. It is clear that the distance of the optical boundaries propagation squared versus time can be well fitted with a linear function. The Eq. (1) allows to determine the diffusion coefficient *D*.

Obtained values of D for different sc CO_2 pressures and temperatures estimated by Eq. (1) are given in Table 1. Plots of the diffusion constants against pressures for different temperatures are presented in Fig. 3a-3b. It can be seen that the diffusion coefficients achieve their maximum values at pressures between 12.5 and 20 MPa depending on the temperature. For the series obtained at different temperatures it was found, that a temperature raising from 38°C to 50°C causes an increase of the maximum diffusion coefficient approximately by a

factor of 1.3. Raising temperatures from 50°C to 55°C and from 55°C to 65°C caused the maximum diffusion coefficients respectively to increase by a factor of 1.5 and 1.9. In Fig. 3c the diffusion coefficients for different pressure series are plotted against the temperature and a similar increase for the maximum diffusion coefficient between the investigated temperatures can be seen. Changing from the lowest temperature, 38°C to the highest 65°C causes the maximum diffusion coefficient to change approximately by a factor of 3.5.
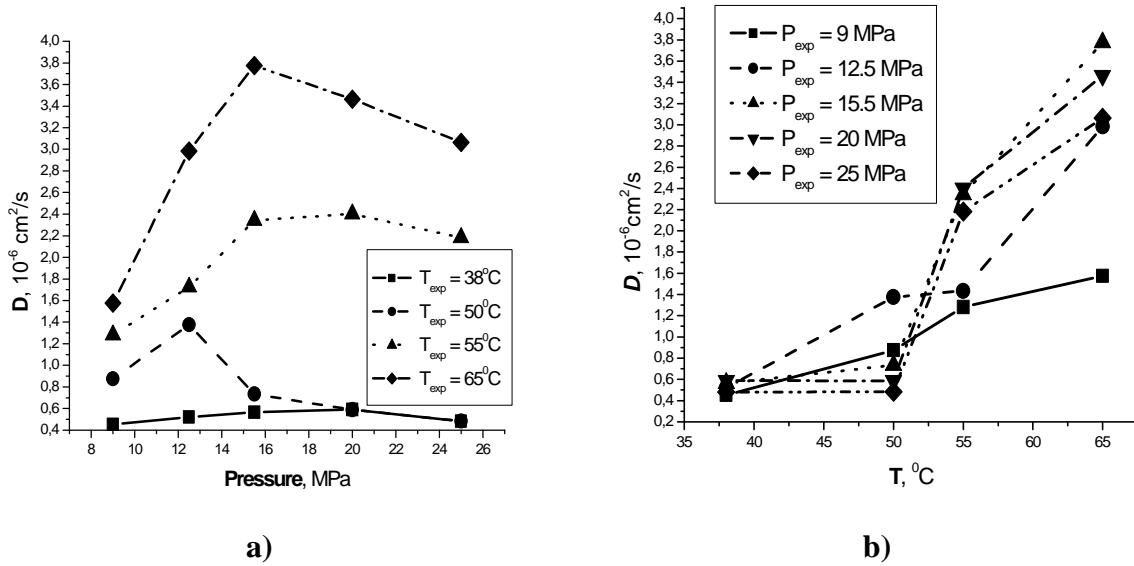

a)   **b)**

Figure 3. Dependences of the diffusion coefficients upon pressure (a) and temperature (b).
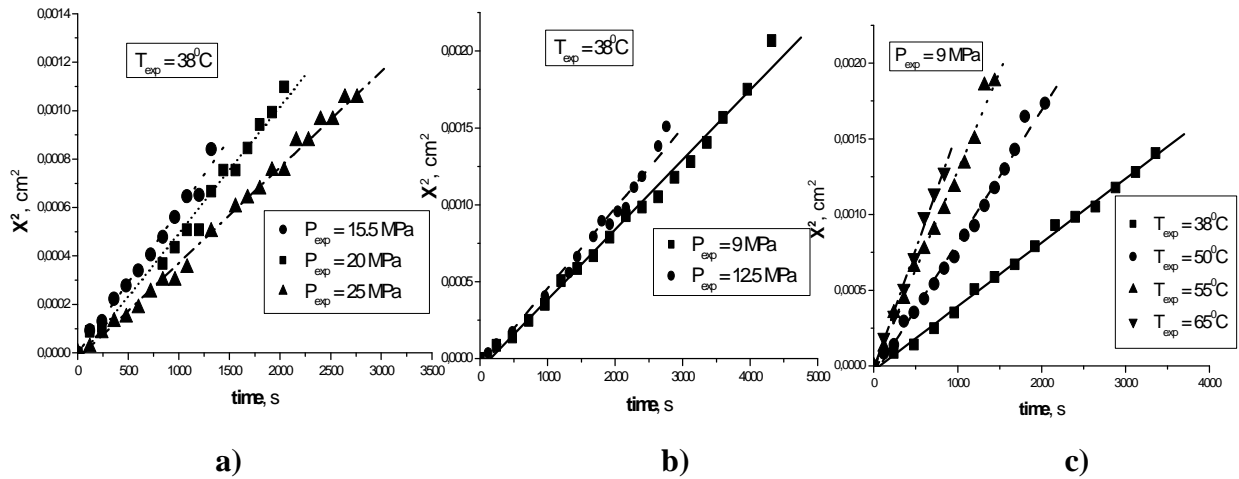

a)   **b)**   **c)**

Figure 2. Typical results of *in situ* observation of the diffusion fronts propagation in PS at different temperatures and pressures.
a), b) Square of the propagation distance of the CO_2 diffusion front in PS samples versus time at temperature t = 38°? and different pressures. c) The same as (a) at pressure 9 MPa and different temperatures.

The presence of the maximum of the *D* in the range of pressures between 12.5 and 20 MPa seems to indicate that under these pressures the favorable conditions for diffusion process may arise. At subsequent increase of the pressure the PS sample seems to be compressed too strongly, which results in decreasing of the efficiency of CO_2 diffusion process.

After the decompression, porous structure with different morphology depending on experiment conditions begins to form. Images of the sample cuts are shown on the Fig. 4. PS samples were cut up to the half of their thickness. Knowing initial dimensions of the sample, one can obtain sections on the fixed distance from the sample edge, study porous structure and measure dependencies of pores diameter as a function of the distance from the sample edge. As can be seen from Fig. 4 morphology of porous structure changes with the pressure change, which can be explained due to penetrant diffusion peculiarities in view of diffusion coefficient alteration. Pores diameters profiles in sample depth for various exposition durations are shown on Fig. 5. As can be seen, longer exposition of PS under supercritical conditions results in formation of pores of smaller diameters. It can be explained due to weaker plastification of PS by the solvent, so during decompression CO_2 are able to produce pores with smaller diameters.
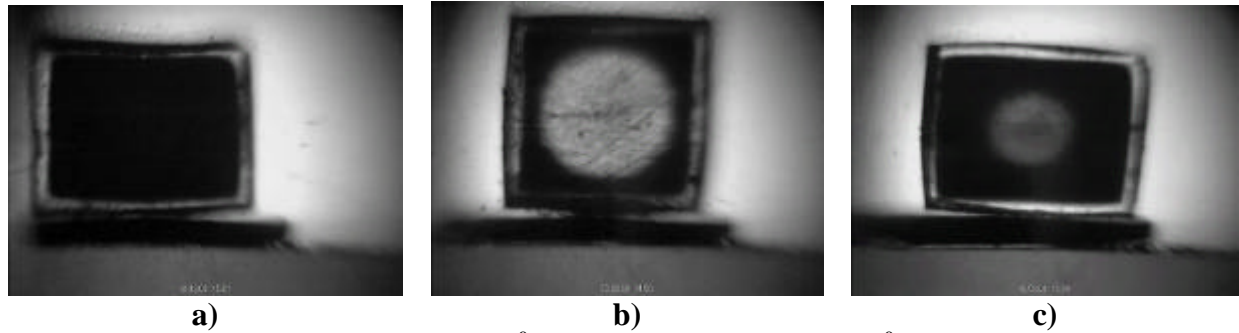

| a) | b) | c) |

Figure 4. Porous structures in PS. a) 38^0? , 15.5 MP?, 3 hours, b) 38^0? , 15.5 MPa, 2.5 hours, c) 38^0? , 20 MPa, 2.5 hours
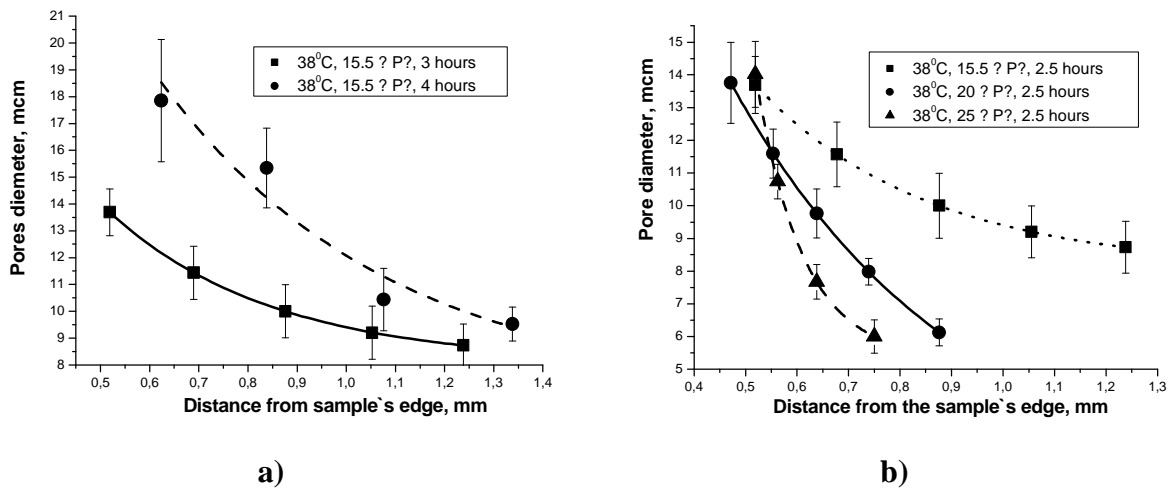

| a) | b) |

Figure 5. Pore diameter profiles in PS for different exposition a) times, b) pressures.

Dependencies of pores diameters for various values of pressure are shown on Fig. 5. Evidently pores diameter decreases with distance from the sample edge and with the exposition pressure, at the same time, the rate of decrease rises. This fact can justified on the basis, that under given exposition conditions equilibrium CO_2 concentration does not settles

on the beginning of the pressure release. In other words, concentration sorbate gradient in sample depth takes place because of the insufficient exposition duration.

According to diffusion theory, CO_2 concentration profile in the sample bears exponential nature. During decompression the most intensive formation of porous structure will proceed in the regions with greater values of sorbate concentration. Since sorbate concentration decreases with distance from the sample edge, then density of porous structure and pores diameter decreases. With increase in exposition pressure, and hence increase in CO_2 density on the moment of decompression, sorbate concentration inside the sample decreases more sharply. So the rate of pores diameter decrease will rise with the increase of exposition pressure.

Thus, it was shown that by adjusting sorption conditions it is possible to produce controlled porous structures with gradient pores size distribution. It has high profile for creation coatings with controlled properties, membranes and adsorbents, capsules for prolonged drugs releasing and many others.

CONCLUSIONS

In this work sorption of supercritical carbon dioxide by PS was studied using optical method. Determination of diffusion coefficients was carried out directly from analysis of propagation of optical boundaries of CO_2 diffusion fronts in PS. The non-monotone diffusion coefficient dependences upon pressure was found out. Optical method allowed direct determination of CO_2 diffusion coefficients in PS.

Processes of porous structure formation in PS during CO_2 desorption were studied. We obtained pores size profiles depending on experiment conditions – pressure, temperature and exposition time of samples in supercritical CO_2. Varying exposition conditions it was found to generate controlled non-uniform porous structures.

REFERENCES

[1] A.I. COOPER, J. Mater. Chem., Vol. 10, **2000**, p. 207.
[2] A. T. YOUNG, Cell. Plastics, **1987**, 23rd Jan., p. 55.
[3] J. S. CHIOU, J. W. BARLOW, D. R. PAUL, J. Appl. Polym. Sci., Vol. 30, **1985**, p. 2633.
[4] S. K. GOEL, E. J. BECKMAN, Cell. Polym., Vol. 12, **1993**, p. 251.
[5] J. R.ROYER, J. M. DeSIMONE, S. A. KHAN, Macromolecules, Vol. 32, **1999**, p. 8965.
[6] J. von SCHNITZLER; R. EGGERS, Journal of Supercritical Fluids, Vol. 16, **1999**, p. 81.
[7] L.N. NIKITIN, E.E. SAID-GALIYEV, R.A. VINOKUR, A.R. KHOKHLOV, M.O. GALLYAMOV, K. SCHAUMBURG, Macromolecules, Vol. 35, **2002**, p. 934.
[8] L.NIKITIN, M.GALLYAMOV, R VINOKUR, A. NIKOLA?V, E. SAID-GALIYEV, A. KHOKHLOV, H. JESPERSEN, K. SCHAUMBURG, J. of Supercritcal Fluids, Vol. 26, **2003**, p. 263